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Thermal Conductivity of Polystyrene:
Selected Values

by

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FOREWORD

This report is the second of a series on the thermal conductivities of materials of scientific and engineering interest. The values selected are based on thorough study and critical evaluation of published investigations. In a critical survey such as this one, much depends on the judgment of the surveyors. The care that the authors of the present survey have exercised may be judged from the comments they have made on the individual papers examined. Their comments on the more important papers are in the text of the report. In addition, they have made many brief comments on less important papers; these comments are given as annotations, immediately following the listing of the paper in the references.

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ABSTRACT

The published literature on the thermal conductivity of polystyrene has been assembled and the results critically evaluated. Best values of thermal conductivity as a function of temperature have been selected. These are presented in both graphical and tabular form; the tables cover the range 240 to 540° K and a few of the plotted points lie outside this range. An attempt was made to consult all work that could significantly affect the choice of best values. Published papers were located with the aid of Chemical Abstracts, Physics Abstracts, the Thermophysical Properties Retrieval Guide, and some other general sources. In addition, relevant references in the papers themselves were followed up until a substantially "closed system" had been generated, as shown by the fact that no new references were being turned up.

THERMAL CONDUCTIVITY OF POLYSTYRENE: SELECTED VALUES

Introduction

Ordinary polystyrene is a transparent, noncrystalline, synthetic, thermoplastic material formed by polymerizing styrene ($C_6H_5\cdot CH=CH_2$). It is marketed under its own name and also under various trade names. Among these are Dylene, Lustrex, and Styron (all U. S.); and Trolitul (German). The trade name is sometimes used for a polystyrene modified by a small amount of additive such as rubber. Code numbers following the names are often used to distinguish the various types of polystyrene. Greater uniformity is to be expected in commercial samples of polystyrene than of many other plastics, because fillers and plasticizers are not often used in polystyrene (24, 25).

The present study does not include expanded (foamed) polystyrene, nor isotactic polystyrene. Expanded polystyrene is formed by the action of gas bubbles generated within the polystyrene while it is liquid. It is an excellent thermal insulator, widely used, but its thermal conductivity is a function of many factors which will not be discussed here. In isotactic polystyrene the phenyl groups, which are attached to every second carbon atom in the molecular chain, are oriented in a regular pattern; whereas in ordinary atactic polystyrene they are random. There appear to be no measurements of the thermal conductivity of isotactic specimens.

Polystyrene is slightly denser than water. Of the workers whose data are plotted in Fig. 1, three gave the densities of their samples; the values ranged from 1.032 to 1.06 g cm^{-3} . Fox and Flory (26) give an equation for the specific volume of polystyrene, from which the density at 25°C is found to be 1.054 g cm^{-3} . Since purified samples were used, this value is probably as reliable as any now available.

The molecular weight of a polystyrene sample has an important influence on its properties. In a table (27) published in 1943, the molecular-weight range of polystyrene for plate castings is given as 250,000 to 400,000; for injection molding, 120,000 to 180,000; and for coatings, 80,000 to 120,000. Modern products may have somewhat lower molecular weights, especially materials for injection molding. The degree of polymerization is found by dividing the molecular weight by 104.144, the molecular weight of a single styrene molecule.

All plastics and rubber-like materials have a glass-transition temperature (also called a second-order transition temperature), below which they are relatively hard and above which they are more soft and

rubber-like. The changes associated with the glass transition do not take place sharply, but are spread over a narrow temperature range. Many of the properties of a polymer show some change at the glass transition. The thermal-conductivity curve of polystyrene shows a change in slope at the glass transition, but the effect is less pronounced than it is in some other high polymers.

The glass-transition temperature of polystyrene depends on its molecular weight. Many equations have been proposed to describe this dependence. That of Fox and Flory (28), relating the glass temperature T_g to the number-average molecular weight M_n is: T_g ("K) = $373 - 1.0 \times 10^5 / M_n$. It gives, for very high molecular weights ($M_n \gg 10^5$), $T_g = 373^\circ\text{K}$ (100°C).

The ordinary (weight-average) molecular weight of commercial samples of polystyrene is above 10^5 , but the number-average is not. This difference is principally due to the presence of monomer, which lowers M_n strongly but has only a minor influence on the weight-average molecular weight. According to Wood (29), commercial samples may contain from 1 to 3 percent of monomer, and may have glass temperatures ranging from 95° to 75°C . Freedom from monomer is to be expected only in specially-purified samples, or possibly in some commercial samples specially made for use at the highest practical temperatures. The presence of low-molecular-weight impurities or additives in polystyrene may be expected to have an effect similar to that of monomer in lowering the glass temperature.

Molecular orientation is known to affect the properties of polymers. Orientation is produced when the material is stretched or caused to flow while hot enough to be somewhat softened. The long axes of the polymer chains tend to line up in the direction of stretch. Density is increased by the orientation. Thermal expansion is decreased in the direction of stretch, and increased in the perpendicular direction. Thermal conductivity k is increased in the direction of stretch and decreased in the perpendicular direction. That is, heat flows more readily along the polymer chains than from one chain to another. For a sample of polystyrene oriented in one direction only, Hellwege, Hennig, and Knappe (13) found at 25°C an increase of 6 percent in the direction of orientation and a decrease of 5 percent in the perpendicular direction, relative to k of the unstretched polymer. This is a smaller effect than that shown by the other high polymers so far reported on. Pasquino and Pilsworth (1) measured unoriented and biaxially-oriented polystyrene. In the oriented sample, heat flow was perpendicular to the plane of orientation, and at 28°C , k was 4 percent less than that of the

unoriented sample. The difference in k of the two samples decreased somewhat with rising temperature. Kargin, Slonimskii, and Lipatov (30) found no dependence of k on direction in a stretched sheet; but their method, which involved the observation of major and minor diameters of regions of melted wax, may not have been sensitive enough to show differences of the order of only a few percent.

Selection of the Values

It was decided to prepare the tables to apply to an unoriented commercial polystyrene having its glass transition at about 358°K (85°C); this temperature corresponds to a monomer content of one percent or so, which is typical of many commercial samples. The accepted curve of thermal conductivity covers the range 240° to 540°K (-33° to 267°C) and is shown by the heavy line in Fig. 1. From 240°K to T_g the curve rises; from T_g to about 400°K the thermal conductivity is constant; and from 400°K upward the curve rises again.

To derive the accepted values, all of the available data were first plotted on a large-scale graph; the more important of these data are shown in Fig. 1. A master curve was then drawn, which after study and revisions was accepted. Table 1 was prepared by reading values from the accepted curve; these values were differenced and smoothed, and then checked against the master curve. Table 2 was derived from Table 1.

As shown in Fig. 1, the selected values follow closely the results of Pasquino and Pilsworth (1), Knappe (2), and Shoulberg (3). The accepted curve agrees well in slope with the data of Kline (4) and Underwood and McTaggart (5). The agreement of Holzmüller and Münx (6), Kirichenko (7), Hager (8), and Williams and Cleereman (9) with the accepted curve is fair to poor, and the agreement of Cherkasova (10), and Holzmüller and Lorenz (11) is definitely poor. The data of Ueberreiter and Nens (12) lie fairly close to the selected curve; however, no great significance should be attached to this fact, for the sample used had a very low molecular weight (3370). The results are included to show the pronounced peak at 345°K (72°C). These authors associate the peak with the glass transition; its location is, in fact, correctly predicted by the equation for T_g given earlier.

Hager's (8) data extend to much lower temperatures than those of anyone else, and it would be normal to give great weight to his low-temperature points. However, when the k -curves of other amorphous polymers, such as poly(methyl methacrylate) and natural rubber, are examined (31), we find that they show much smaller

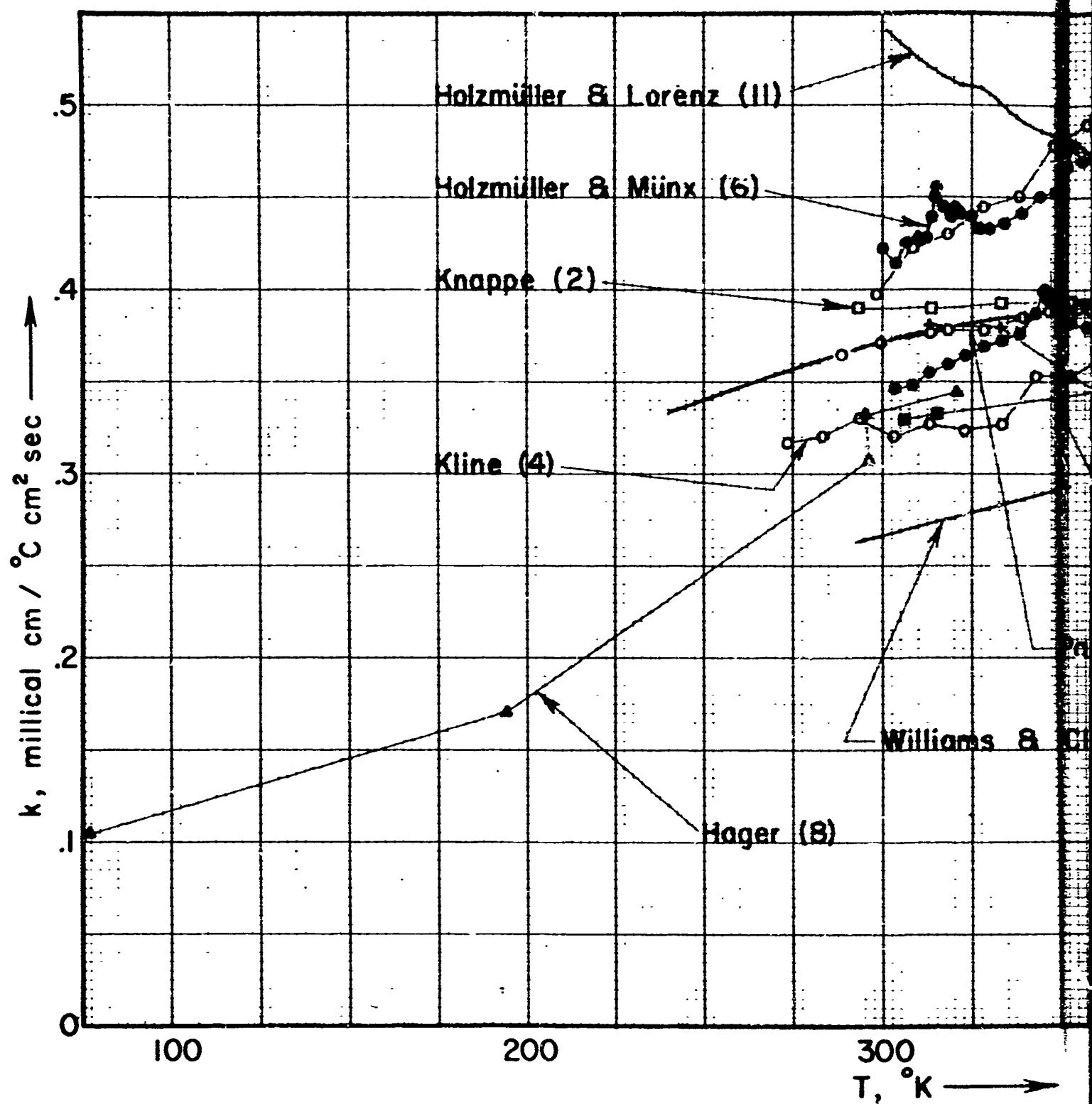
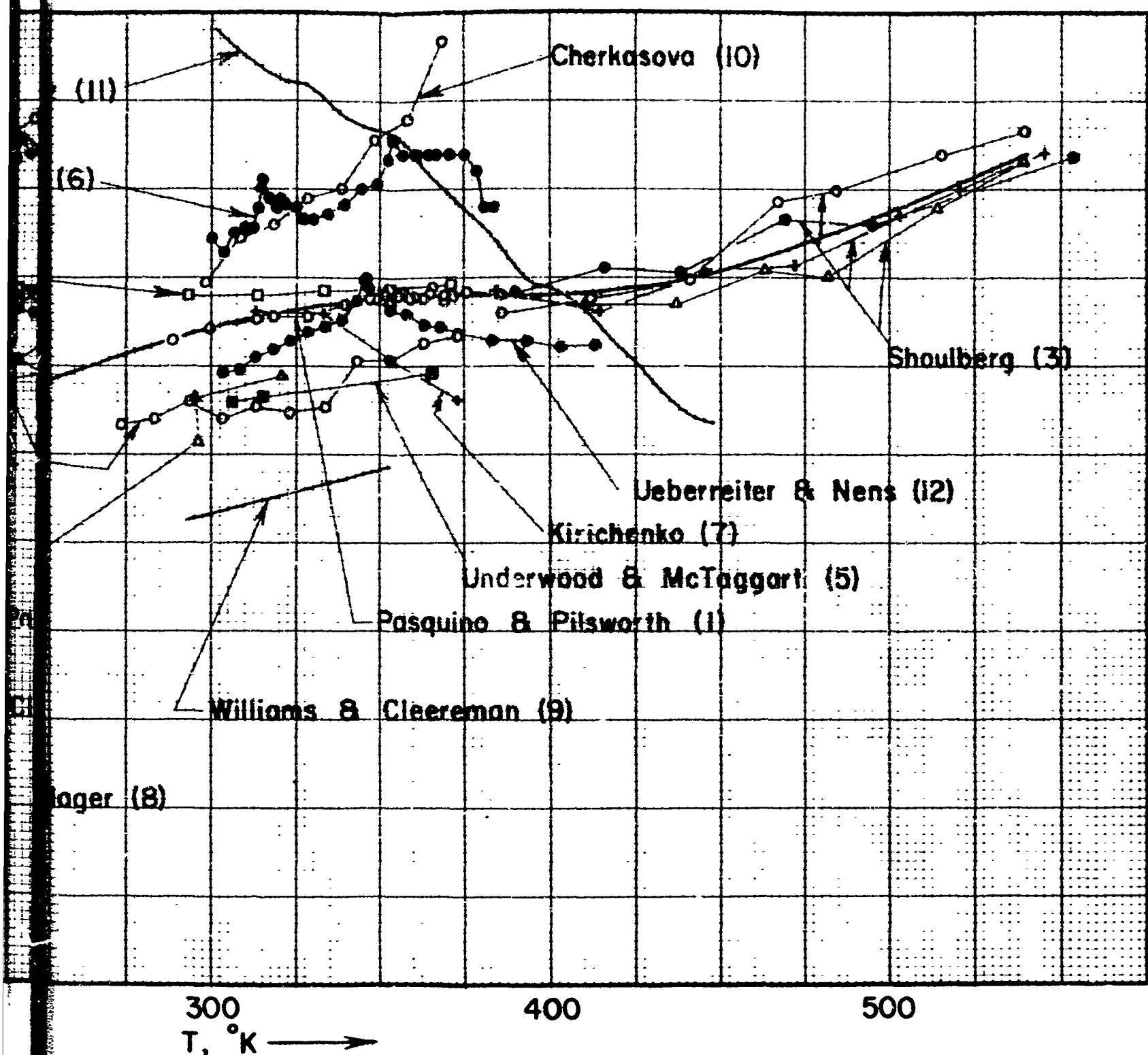


Fig. 1. Thermal-conductivity data of references (1) to (12). The



be of references (1) to (12). The heavy line represents the selected values.

B

Thermal conductivity of volystyrene

Table 1

T °K	α millical cm sec °C
240	0.333
260	.347
280	.360
300	.372
320	.380
340	.386
360	.389
380	.390
400	.390
420	.393
440	.399
460	.410
480	.423
500	.437
520	.453
540	.470

Table 2

T °R	k Btu in. °R ft ² hr
450	0.99
500	1.04
550	1.09
600	1.12
650	1.13
700	1.13
750	1.14
800	1.16
850	1.21
900	1.27
950	1.33

percentage drops in k with temperature than Hager's data. Since theoretical considerations also predict a relatively small temperature-dependence of k in amorphous materials as compared with crystalline materials, we have been unwilling to use Hager's lowest points as the basis for accepted values, and have stopped the master curve at 240°K.

The selected values above 400°K are almost entirely based on the work of Shoulberg (3). Both Shoulberg and Kirichenko (7) reported thermal diffusivity (α) rather than k -values. The plotted k -values were computed from their data as explained later. Shoulberg worked in a range where polystyrene softens and special techniques are necessary. This fact, and the uncertainties introduced by calculating k from α , necessarily reduce the probable accuracy of his results; the data do, however, join smoothly with the accepted values at lower temperatures.

The calculation of thermal conductivities from thermal diffusivities is based on the equation $k = \alpha \rho c_p$, where ρ is density and c_p is specific heat at constant pressure. We have computed densities from the specific-volume data of Fox and Flory (26), using the equation $v = 0.00025 t$ (°C) + 0.943 below the glass temperature; $v = 0.00055 t$ (°C) + 0.913 between the glass temperature and 160°C (433°K); and $v = 0.000715 t$ (°C) + 0.887 at and above 160°C. Specific heats were taken from the tabulated data of Brickwedde as reported by Stull (32) up to the limit of the table (400°K). At higher temperatures a linear extrapolation of this table, c_p (cal g⁻¹ deg⁻¹) = 0.00112 T (°K) + 0.0185 was used, after comparing the extrapolation with the curve of Stull as reported by Williams and Cleereman (9).

Further information bearing on the accuracy of the plotted data is given in the annotations to the references. In addition to the papers represented in Fig. 1, there are a number of others that contain k -data for polystyrene. These papers are listed in the second group of references. They are also annotated, and it is usually clear from the annotation why the results were not plotted in Fig. 1. Some sets of data have been omitted because we believe they contain large experimental errors. In other cases the work may have been quite accurate, but only a single value has been reported. Such isolated values have been omitted to avoid crowding in the figure, but were given some weight when the selected values were chosen.

Reliability of the Tables

Variations in the thermal-conductivity values reported for polystyrene by different investigators are larger than the apparent

uniformity of commercial material would suggest. Among the possible causes of these variations are the existence of orientation introduced during manufacture; and differences in glass-transition temperature caused principally by unpolymerized styrene. The thermal history of the sample may possibly have some effect on k . The experience of Pasquino and Pilsworth indicates that shrinkage and warping of polystyrene may occur near and above the glass transition. This warping can easily cause errors in measurements, even when there is actually no change in k .

The tabulated values of k are believed to be correct within ± 6 percent from room temperature to 393°K (120°C). Outside this range the uncertainty increases: at 240°K , the lower limit of Table 1, it is probably ± 10 percent; and at 540°K , the upper limit of Table 1, it is probably ± 12 percent.

Data for Conversion of Units

$$T\ (^{\circ}\text{R}) = T\ (^{\circ}\text{K}) \times 1.8.$$

$$T\ (^{\circ}\text{K}) = t\ (^{\circ}\text{C}) + 273.15.$$

$$T\ (^{\circ}\text{R}) = t\ (^{\circ}\text{F}) + 459.67.$$

$$\text{Watt cm } ^{\circ}\text{K}^{-1}\text{cm}^{-2} = \text{cal cm } ^{\circ}\text{K}^{-1}\text{cm}^{-2}\text{sec}^{-1} \times 4.1840.$$

$$\text{Btu in. } ^{\circ}\text{R}^{-1}\text{ft}^{-2}\text{hr}^{-1} = \text{cal cm } ^{\circ}\text{K}^{-1}\text{cm}^{-2}\text{sec}^{-1} \times 2902.9.$$

$$\text{Btu ft } ^{\circ}\text{R}^{-1}\text{ft}^{-2}\text{hr}^{-1} = \text{cal cm } ^{\circ}\text{K}^{-1}\text{cm}^{-2}\text{sec}^{-1} \times 241.91.$$

References

Containing data plotted in Fig. 1.

1. Anne D. Pasquino and Malcolm N. Pilsworth, Jr., "The thermal conductivity of polystyrene, oriented and unoriented, with measurements of the glass-transition temperature," *Polymer Letters* 2, 253-5 (1964). The k-values were obtained by the guarded-hot-plate technique, and are considered to be accurate to \pm 2 percent.
2. W. Knappe, "Steady-state absolute measurements of the thermal conductivity of technical high polymers in the temperature range from 20° to 100°C," *Kunststoffe* 51, 707-8 (1961). A thin-foil heater between two samples was used, in an arrangement requiring no guard ring.
3. Robert H. Shoulberg, "The thermal diffusivity of polymer melts," *J. Appl. Polymer Sci.* 7, 1597-611 (1963). Each sample consisted of two disks with a thermocouple between them, entirely surrounded by heavy walls. Gas pressure was used to force the sample into good thermal contact with the walls. Four of the five samples measured were essentially pure polystyrene, and the results are shown in Fig. 1. The fifth sample was Styron 700; this material according to Dr. Daniel R. Stull (private communication) contains about 20 percent of α -methyl-styrene. Data for this sample were therefore omitted, although they did not differ noticeably from the data for the other samples.
4. Donald E. Kline, "Thermal conductivity studies of polymers," *J. Polymer Sci.* 50, 441-50 (1961). A steady-state method was used with a coaxial-cylinder apparatus.
5. W. M. Underwood and R. B. McTaggart, "The thermal conductivity of several plastics, measured by an unsteady state method," *Chem. Eng. Progr. Symposium Ser.* 56, No. 30, 261-8 (Storrs Symposium, 1959). The experimental points obtained by these authors were not given; the results were represented by a curve. Since this curve shows no details of the behavior of k near T_g it is not shown in Fig. 1. Instead we have shown the three experimental points obtained for Underwood and McTaggart by a commercial testing laboratory, using a "conventional A. S. T. M. method."

6. W. Holzmüller and M. Münx, "Temperature dependence of the thermal conductivity of macromolecular substances," *Kolloid-Z.* 159, 25-8 (1958). A guarded-hot-plate method was used, with a rather small temperature difference across the sample.
7. Yu. A. Kirichenko, "The determination of thermophysical characteristics by the method of radial temperature waves," *Teplo i Massoperenos, Pervoe Vses. Soveshch.*, Minsk, 1, 77-85 (1961). A cylindrical sample was used, with thermocouples or resistance thermometers at the axis and at various distances from the axis. The radial temperature waves were generated by a heater outside the sample.
8. Nathaniel E. Hager, Jr., "Thin-heater thermal conductivity apparatus," *Rev. Sci. Instr.* 31, 177-85 (1960). Two of the five k-values were obtained by a comparison method; the other three were obtained in a hot-plate apparatus that utilized a heater thin enough to make a guard ring unnecessary.
9. J. L. Williams and K. J. Cleereman, in Styrene, its polymers, copolymers, and derivatives, Ray H. Boundy and Raymond F. Boyer, editors, Reinhold Publishing Corporation, New York (1952), p. 479. The data are unpublished work of Stull, presented in the form of a straight-line graph.
10. L. N. Cherkasova, "Effect of structure on the thermal conductivity of polymers," *Russian J. Phys. Chem.* 33, 9, 224-6 (1959). The methods employed in this work are not fully described. For polystyrene, one of the reported quantities is a logarithmic cooling rate; hence a steady-state method was not used.
11. W. Holzmüller and J. Lorenz, "Thermal conductivity of thermoplastics in the softening region," *Plaste und Kautschuk* 8, 351-2 (1961). A steady-state absolute method was used. To permit reliable measurements on materials that were softening, the apparatus utilized an aluminum apparatus somewhat like a cylinder and piston, inside which the sample could be compressed. Two samples were used, with the heater sandwiched between them.
12. K. Ueberreiter and S. Nens, "Specific heat, specific volume, thermal diffusivity, and thermal conductivity of high polymers. Part I."

Distyrene and a high-polymer polystyrene," *Kolloid-Z.* 123, 92-9 (1951). These authors used a cylindrical sample with a thermocouple at the axis, and measured α , c_p , and ρ , from which k was calculated. Only qualitative accuracy is claimed for the results.

Containing data not plotted in Fig. 1.

These references contain the data judged to be less important than those in references (1) to (12). Each of the references in this group is followed by a brief annotation, in which the k -values reported in the paper are included. Numerical values given below are in $\text{cal cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$.

13. K. H. Hellwege, J. Hennig, and W. Knappe, "Anisotropy of thermal expansion and heat conduction in unidirectionally-stretched amorphous high polymers," *Kolloid-Z. und Z. für Polymere* 188, 121-7 (1963). Their primary interest was in the effect of stretching; however, they give a good measured value for unstretched polystyrene (Trolitul III), $k = 0.000389$ at 25°C .
14. Makoto Hattori, "Heat conduction in some linear polymers," *Bull. Univ. Osaka Prefecture Ser. A*, 9, 1, 51-8 (1960). The measurements on polystyrene were made with an unguarded-hot-plate apparatus. The data show a steep rise at about 350°K . We have assumed that some sort of error was present and have not included the data in Fig. 1.
15. Paul K. Chung and Melbourne L. Jackson, "Thermal diffusivity of low-conductivity materials," *Ind. Eng. Chem.* 46, 2563-6 (1954). Three values of α are reported, from which we have computed k by the method described in the text of this report. The temperature was assumed to be 25°C , and the k -values found are 0.000406, 0.000406, and 0.000409.
16. Kurt Ueberreiter and Evelyn Otto-Laupenmühlen, "Specific heat, specific volume, thermal diffusivity, and thermal conductivity of high polymers. Part II. Chain-length dependence for fractionated polystyrenes," *Z. Naturforsch.* 8a, 664-73 (1953). This paper is more recent than that of Ueberreiter and Nens (12). However, the curves of k vs. temperature show a rather complicated behavior in the neighborhood of the glass transition, a behavior which has not yet been confirmed by other observers.

17. W. C. Goggin, "The polystyrene family," ASTM Symposium on Plastics, Am. Soc. for Testing Materials, Philadelphia (1944), p. 178-87. Gives a single, very low value for polystyrene, $k = 0.00019$, but does not give the temperature nor method.
18. S. Erk, A. Keller, and H. Poltz, "Thermal conductivity of synthetic materials," Physik. Z. 38, 394-402 (1937). A good single determination at the Physikalisch-Technische Reichsanstalt by a comparison method is reported: $k = 0.000375$ at 36°C . The density was measured and found to be 1.053 g cm^{-3} .

Containing data for which another reference is preferred.

19. A. Jacobs and D. E. Kline, "Energy deposition in polymers by reactor radiation," J. Appl. Polymer Sci. 6, 605-12 (1962). Reference (4) is fuller and is preferred.
20. Werner Knappe, "Determination of the thermal properties of badly-conducting materials with a two-sample apparatus without a guard ring," Z. angew. Physik 12, 508-14 (1960). Reference (2) is preferred. However, the present paper contains a better description of the apparatus and experimental techniques employed.
21. L. N. Cherkasova, "Effect of structure on the thermal conductivity of polymers," Zhur. Fiz. Khim. 33, 1928-32 (1959). This is the Russian original of reference (10).
22. Makoto Hattori and Osamu Kamiike, "Studies on thermal conductivities of high polymers. II. Thermal conductivities of polystyrene and polyethylene," Kobunshi Kagaku 15, 285-7 (1958). In Japanese with English abstract. Reference (14) is preferred.
23. S. Erk and A. Keller, "Heat conduction by synthetic resins. Information on the activity of the Physikalisch-Technische Reichsanstalt 1935," Physik. Z. 37, 306 (1936). This paper appears to be a preliminary report of what was given in reference (18), which is preferred.

Containing no thermal-conductivity data on polystyrene.

24. Brage Golding, Polymers and resins. Their chemistry and chemical engineering, D. Van Nostrand Company, Inc., Princeton, New Jersey (1959), p. 514.

25. J. L. Williams and K. J. Cleereman, reference (9), p. 496 and 506.
26. Thomas G. Fox, Jr., and Paul J. Flory, "Second-order transition temperatures and related properties of polystyrene. I. Influence of molecular weight," *J. Appl. Phys.* 21, 581-91 (1950).
27. H. Mark, "Some scientific aspects of the synthetic rubber problem," *Am. Scientist* 31, 97-141 (1943).
28. Thomas G. Fox and Paul J. Flory, "The glass temperature and related properties of polystyrene. Influence of molecular weight," *J. Polymer Sci.* 14, 315-9 (1954).
29. Lawrence A. Wood, in Synthetic rubber, G. S. Whitby, editor, John Wiley and Sons, New York (1954), p. 357.
30. V. A. Kargin, G. L. Slonimskii, and Yu. S. Lipatov, "Heat propagation in oriented polymers," *Doklady Akad. Nauk SSSR* 104, 96-7 (1955).
31. K. Eiermann, "Heat conduction of plastics and its dependence on structure, temperature, and previous history," *Kunststoffe* 51, 512-7 (1961).
32. D. R. Stull, in Styrene, its polymers, copolymers, and derivatives, Ray H. Boundy and Raymond F. Boyer, editors, Reinhold Publishing Corporation, New York (1952), p. 67.

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Heat transfer	8					
Styrene plastics	9		9		9	
Polymers	9		9		9	
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14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

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